14. ^{15}N-NMR Spectroscopic Characterization of Triaziridines

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The ^{15}N-NMR spectra of *cis*- and *trans*-2,3-dialkyl-substituted triaziridines are reported. The assignment of the ^{15}N-NMR resonances is described, and the chemical-shift and coupling data are compared with those of aziridines and diaziridines. The ^1J(N,H) coupling constants allow one to deduce the relative configuration of the involved N-atom. In CDCl$_3$, a ^1J(N,H) value of 58.1 ± 0.5 Hz is assigned to an N–H bond *cis* to two lone-pairs of electrons at neighboring N-atoms, *i.e.* to the *cis,trans*-triaziridines[1]), and a value of 51.7 ± 0.5 Hz is assigned to a N–H bond *cis* to only one lone-pair of electrons, *i.e.* to *trans,cis*-triaziridines[1]).

1. Introduction. – The synthesis of small-membered strained rings has always been a special challenge for chemists. Among these rings, the one with three N-atoms in a cycle has not been prepared until recently. In 1977, a first report appeared on the isolation of a silver complex of triazacyclopropane, *i.e.* triaziridine, in Zeolite A [1], and since 1980 *Dreiding et al.* reported on the successful synthesis of triaziridines of type **A** and type **B** [2–5]. Very recently, another paper about triaziridines has appeared [6].
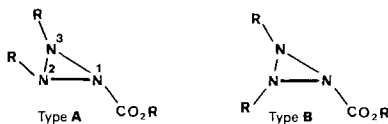
These syntheses are based on a photochemical cyclization of suitably substituted azimines, R–N=N(R)=N–COOR. Extensive use of NMR-spectroscopic methods allowed the deduction of the constitution and the relative configuration of N(2) and N(3) of the triaziridines **A** and **B** [3] [5]. It was shown that all N-atoms are pyramidal and that inversion of N(2) and N(3) is slow at temperatures where the three-membered ring remains intact. Inversion of N(1) was found to be somewhat faster and, for type-**B** triaziridines, could be followed by temperature-dependent ^{1}H- and ^{13}C-NMR spectroscopy; an activation energy of *ca.* 62 kJ/mol was measured.

Here we report on the ^{15}N-NMR spectra of eight triaziridines for further characterization of this novel class of compounds and to compare the date with those of aziridines and diaziridines.

2. ^{15}N-NMR Data of Triaziridines. – It appears only logical that ^{15}N-NMR spectroscopy provides the most appropriate method for the structural proof of a three-membered N-homocycle since the symmetry of the structures involved as well as the difference to the educt molecules of the synthesis are expected to show up clearly by this method. The compounds with sufficient thermal stability were measured at an ambient temperature of 24°. The temperature was lowered when ring-opening reactions were known to occur

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[1])   The first stereodescriptor denotes the relative configuration of the two equal alkyl substituents, the second the relative configuration of one alkyl substituent and the H-atom.

Table 1. ^{15}N-NMR Chemical Shifts[a]) of Triaziridines

Compound	Solvent	Temp.	N(1)	N(2)	N(3)
1	CDCl$_3$	– 24°	119.9 (– 260.3)	144.0 (– 236.2)	144.0 (– 236.2)
2	CDCl$_3$	– 27°	145.0 (– 235.2)	164.9 (– 215.3)	164.9 (– 215.3)
3	CDCl$_3$	24°	131.1 (– 249.1)	141.2 (– 239.0)[b])	139.0 (– 241.2)[b])
4	CDCl$_3$	– 22°	155.4 (– 224.8)	166.8 (– 213.4)	153.0 (– 227.2)
5	CDCl$_3$	24°	94.8 (– 285.4)	119.4 (– 260.8)	119.4 (– 260.8)
	(CD$_3$)$_2$SO	24°	95.4 (– 285.8)	119.0 (– 261.2)	119.0 (– 261.2)
6	CDCl$_3$	– 20°	119.3 (– 260.9)	139.1 (– 241.1)	139.1 (– 241.1)
7	CDCl$_3$	24°	104.5 (– 275.7)	138.4 (– 241.8)	138.4 (– 241.8)
8	CDCl$_3$	24°	116.8 (– 263.4)	132.2 (– 248.0)	132.2 (– 248.0)

[a]) δ [ppm] relative to liquid NH$_3$: δ(NH$_3$) = δ(CH$_3$NO$_2$) + 380.2 ppm; values in parenthesis relative to CH$_3$NO$_2$.
[b])   Assignment tentative, see text.

1 R = H
2 R = CO$_2$CH$_3$

3 R = H
4 R = CO$_2$CH$_3$

5 R = H
6 R = CO$_2$CH$_3$
7 R = CH$_3$
8 R = CH$_2$OH
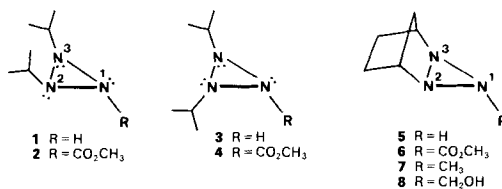
during the course of the measurement or when an unfavourable coalescence point due to an intermediate rate of N(1) inversion had to be expected at 24°.
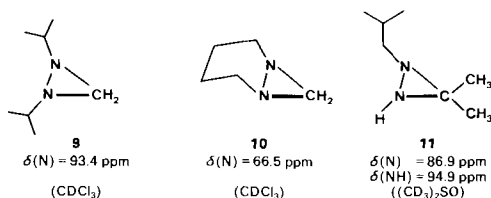
2.1. *Chemical Shifts*. The chemical shifts of the triaziridines **1** to **8** are given in *Table 1*.

The occurrence of three N-resonances requires that the equal substituents at N(2) and N(3) on the triaziridine ring are *trans*-situated in all cases and that N(1) inversion is slow on the NMR-time scale at the temperature indicated. This is also supported by the ^{13}C-NMR spectra at similar temperatures of compounds **3** and **4** which show 4 signals for the CH$_3$ groups and 2 signals for the CH groups of the isopropyl substituents. The compounds **5–8** must have the substituents at N(2) and N(3) in a *cis*-arrangement due to the ring strain and, thus, the observation of only 2 ^{15}N-resonances must be due to either rapid inversion at N(1) or slow inversion and almost exclusive population of one of the two possible interconverting N(1) configurational isomers. The latter possibility certainly holds for R = alkyl, since the assumption of an inverting N-atom (even slowly) would also imply the isomerization of a *cis*- to a *trans*-triaziridine in the monocyclic series, which has never been observed under the experimental conditions of NMR measurements, and it also holds for R = CO$_2$CH$_3$ since in **4** the inversion at N(1) manifested itself in the ^{13}C-NMR spectrum only at a more elevated temperature [3]. Steric arguments suggest the N(1) substituent in **6–8** to be predominantly in an *exo*-position, a situation found in the crystal structure of compound **6** [7]. For R = H, the dominant configuration is less clearly indicated since the stereo-differentiating capabilities of an N lone-pair *versus* an N–H bond are less obvious. The correctness of the configuration shown in the formula will follow from an analysis of the N–H coupling constant *(Chap. 2.2)*. The occurrence of only 2 ^{15}N-NMR resonances as observed for the tricyclic compounds **5–8** is considered indicative for all N(2),N(3) *cis* compounds, *i.e.* also for **1** and **2**.

The ^{15}N-NMR signals of the *cis*-compounds having C_s symmetry were assigned by the line intensities. The signals of N-atoms carrying an H-atom could be identified by their ^1J(N,H) coupling constant. This parameter was measured by application of the po-

larization-transfer pulse sequence INEPT [8]. By such an experiment, also the resonances of N(2) and N(3) in **2** and **4** could be enhanced and thus be distinguished from the N(1) resonance, whereby the polarization transfer was achieved mainly through the N,H coupling to the CH_3 protons (^3J(N,H)). The resulting enhanced up-down signal, however, could not be analyzed unambiguously in terms of long-range N,H-coupling constants. We are then left with the problem of differentiating between N(2) and N(3) in the 2,3-*trans* compound **3** and **4**. If we imagine compound **4** as being obtained from **2** by an inversion of N(2), we note that this process places the substituent at N(1), R=CO_2CH_3, *cis* to the substituent at N(2) so that the lone-pair at N(1) becomes *cis*-placed to the lone-pair at N(2). On the other hand, the substituent at N(3) looses a *cis*-placed substituent so that the lone-pair at N(3) no longer has a *cis*-placed lone-pair at N(2). As a result of this fictitious N(2) inversion, one can expect the signals of N(1) and N(3) to move in opposite directions in going from **2** to **4**. The signal of N(1) in **4**, already assigned as shown, has moved by +11.1 ppm, and one of the two remaining signals is indeed found shifted by −11.9 ppm with respect to the corresponding signal in **2** and assigned to N(3). The third resonance of **4** is almost unaffected (+1.9 ppm) and thus attributed to N(2). The almost identical value for the up- and down-frequency shifts discussed above is certainly accidental and possibly due to the comparable size of the three N-substituents. This situation is not encountered for the pair **3** and **1** so that here the assignments of N(2) and N(3), based on δ-value shifts in going from **1** to **3**, are less certain. These shifts are: $\Delta\delta$(N(1)) = 11.2, $\Delta\delta$(N(3)) = −5.0, and $\Delta\delta$(N(2)) = −2.8 ppm.

The N-chemical shifts of our triaziridines extend over the rather broad range of 94 to 167 ppm. Alkylaziridines have δ-values of 0–35 ppm [9] and hydrazines, including pyrazolines, absorb between 72 and 125 ppm [10], a range overlapping with that of the triaziridines. Only a few δ-values have been reported for diaziridines, *e.g.* 75.9 ppm for δ(NH) of 1,3,3-trimethyldiaziridine [11]. The ^{15}N-NMR data we obtained for the two

9
δ(N) = 93.4 ppm

(CDCl₃)

10
δ(N) = 66.5 ppm

(CDCl₃)

11
δ(N) = 86.9 ppm
δ(NH) = 94.9 ppm
((CD₃)₂SO)

diaziridines **9** and **10** may serve as a better comparison to *cis*- and *trans*-triaziridines, respectively. Replacement of CH_2 by NH in the three-membered ring in going from **9** to **3** deshields the N-atoms by about 47 ppm. A similar effect of 52 ppm is observed for the pair **10** (bicyclic) and **5** (tricyclic). Comparison of **5** with **1** and of **6** with **2** reveals that a shielding effect of about −25 ppm occurs on N(2),N(3) when their two *cis*-substituents are tied together in a ring. The same effect must also be responsible for the large difference in the δ(N) values of **9** and **10**. The α-substituent effect of the CO_2CH_3 groups is +25 ppm in all three cases and can be compared with the effect found in going from $(CH_3)_2N-H$ to $(CH_3)_2N-CO_2CH_2CH_3$, which is +55 ppm. We interpret this large difference in α-substituent effect as being due to a difference in the interaction of the N lone-pair and the alkoxycarbonyl group, *i.e.* a conjugation limited in the triaziridines because of the pyramidality of the N-atom, nevertheless sufficient for the CO_2CH_3 group to lower the barrier of N(1) inversion by stabilizing the planar transition state.

Finally, we would like to report the chemical shifts of the azimine **12**, the synthetic precursor of the triaziridine **6**: 235.6, 339.7, and 366.5 ppm.

12
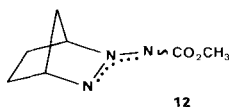
2.2. $^1J(N,H)$ *Coupling Constants.* The measurement of N,H-coupling constants may provide information about N-hybridization and the relative configuration at N(1). Typical $^1J(N,H)$ values of triligant sp^2 N-atoms are 85 ± 8 Hz (*e.g.* aniline in $CDCl_3$: 78.0 Hz; *N*-methylacetamide in DMSO: 93.0 Hz) [11], being about 3–4 Hz larger in DMSO than in $CDCl_3$ solutions. For imines, *i.e.* biligant sp^2 N-atoms, these values are *ca.* 51 Hz [12] and for pyramidal sp^3 N-atoms about 64 Hz in the gas phase [11]. Almost no data are available for alkyl-substituted amines in solution because rapid intermolecular NH exchange 'washes out' the NH coupling. We, too, were not able to determine $^1J(N,H)$ of 2-ethylaziridine; neither in DMSO solution at 10° nor in CD_2Cl_2 at $-90°$ and $B_o = 9.4\ T$ was the exchange rate sufficiently low. In order to get an idea about the $^1J(N,H)$ coupling constants to be expected in a three-membered ring, we first looked at the $^1J(C,H)$ coupling constants in the following model systems:
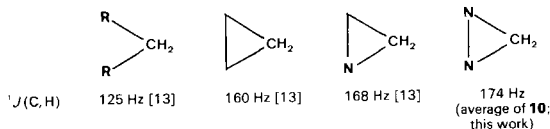
A 30% increase in $^1J(C,H)$ is observed as a three-membered-ring effect and a further moderate increase by the introduction of electronegative N-atoms. Similarly, from the data of *Table 2*, the following model series for $^1J(N,H)$ can be constructed:
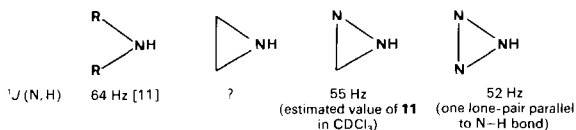

Table 2. $^{15}N, ^1H$-*Coupling Constants* $^1J\,(\pm\,0.5$ Hz)

		1	3	5	11
$^1J\,(N,H)$	$CDCl_3$	58.1	51.7	58.1	
$^1J\,(N,H)$	$(CD_3)_2SO$			61.8	58.8

We note no three-membered-ring effects with $^1J(N,H)$ coupling constants as with $^1J(C,H)$. A possible explanation is that closing the ring does not lead to an increase of the s-character of the N-orbital binding the H-atom, as it is the case for the C-orbital, but instead to an increase of its p-character at the expense of the lone-pair orbital which would have increased s-character. This picture also helps to explain the finding that so far no pK_b-value could be measured for the triaziridines **1**, **3**, and **5** under ordinary conditions[2]) suggesting a rather low basicity of these compounds. It is also consistent with

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[2]) Titration with aqueous HCl ($c = 0.1$ mol/l) in $EtOH/H_2O$ 1:1.

geometry calculations on 3-methyldiaziridine obtained from electron-diffraction data [14], which show that the H-atoms at the N- and C-atoms are located at quite different angles with respect to the plane of the ring:
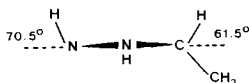
The influence of the electronegativity of the neighbor N-atoms on $^1J(N,H)$ is not clearly visible from the limited data but seems to be small. The observed difference in $^1J(N,H)$ between N(2),N(3) *cis*- and *trans*-substituted systems, however, is highly significant, and we interpret this finding with a reasoning generally accepted in ^{13}C-NMR spectroscopy [13] and justified theoretically [15], namely that N-lone-pair electrons *cis* to a C—H bond increase and *trans* to a C—H bond decrease the respective $^1J(C,H)$ coupling constant (compare, *e.g.*, the two $^1J(C,H)$ values of 181 Hz and 166 Hz observed in **10**). Thus, since the *cis*-substituted triaziridines show larger $^1J(N,H)$ coupling constants than the *trans*-isomers, we conclude that the N—H bond in **1** and **5** is synperiplanar to two lone-pairs and that, therefore, the configuration at N(1) is indeed as indicated in the formula, also in the case of R = H. The preference of this configuration may either be due to steric reasons (N—H bond bulkier than lone-pair) or, more likely, to the absence of unfavourable lone-pair to lone-pair interactions.

3. Experimental. – As for the synthesis of the compounds, see the following references: **2** [5], **4** and **6** [3], **1**, **3**, **5**, **7** and **8** [16], **9** and **10** [17], and **11** [18].

The ^{15}N-NMR spectra were recorded at 20.3 MHz *(Varian XL-200)* or 40.6 MHz *(Bruker AM-400)*. The polarization-transfer methods DEPT [19] for noise-decoupled and INEPT [7] for coupled spectra were used for appropriate resonances. Cr(acac)$_3$ was added to the solns. (< 0.1 mol/l) in order to obtain all ^{15}N-NMR resonances. The resonance position of CH$_3$NO$_2$ in a capillary was determined for Cr(acac)$_3$-free solns. and used as a standard. Chemical shifts are referenced to liquid NH$_3$ by converting the CH$_3$NO$_2$ values according to the relation: $\delta(NH_3) = \delta(CH_3NO_2) + 380.2$ ppm without susceptibility corrections. The reproducibility is estimated to be ±0.5 ppm for chemical shifts and ±0.5 Hz for coupling constants.

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